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(54) New catalyst components for the polymerization of ethylene and of mixtures thereof with olefins and catalysts obtained therefrom.

(57) Components of catalysts for the polymerization of ethylene and of mixtures thereof with olefins, in the form of emulsions or dispersions in an inert liquid medium or in inert gas phase of a liquid phase comprising a compound or composition containing a compound of the metals of the Groups IV to VI of the Periodic System, immiscible in aliphatic hydrocarbons or which components are obtained from emulsions or dispersions in an inert liquid medium or in gas phase of a precursor of the catalyst component, which in the liquid state is immiscible with the normal aliphatic hydrocarbons.

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COMPLETE DOCUMENT



5       Object of this invention are new catalyst components for  
the polymerization of ethylene and of the mixtures thereof  
with olefins and the catalysts obtained therefrom.

10       More particularly, the invention refers to new liquid  
catalytic components used in emulsion or dispersion in an  
inert liquid medium and the use of the catalysts deriving  
therefrom in the polymerization of ethylene and of mixtures  
thereof with alpha-olefins and/or with polyenes containing  
at least two double bonds.

15       It is known that the coordination catalysts commonly  
used in the industrial practice are heterogeneous systems ob-  
tained by reaction of a transition metal compound (generally  
a Ti halide) with an organometal compound of the metals of  
Groups I to III of the Periodic System.

20       The transition metal compound used for the preparation  
of the catalyst is generally a solid insoluble in the hydro-  
carbon polymerization medium or is a liquid soluble in said  
medium.

25       Homogeneous coordination catalysts (soluble in the poly-  
merization medium at least before the polymerization is  
started) are also known.

30       These systems, however, have not been adopted in the in-  
dustrial practice because of the fact that the activity  
thereof, that at the beginning is also very high, decreases  
rapidly and this does not allow to obtain high polymer  
yields.

35       Within the field of heterogeneous catalysts, supported

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5 catalysts have been adopted in the industrial practice already since some time, which are endowed of so high acti  
10 ty as to allow to avoid the expensive depuration treatments of the polymer from the catalytic residues. These catalysts are generally obtained from a catalyst component comprising a titanium compound supported on a magnesium halide in ac-  
15 tive form.

In the modern industrial processes using "high yield" supported catalysts the requirement is felt of having available  
15 catalysts with controlled morphology and particle size, capable to yield a polymer in form of particles reproducing the morphology and the particle size of the catalyst and fur  
20 thermore endowed with high flowability and bulk density.

A catalyst having these characteristics shows advantages not only during polymerization step and makes easier  
25 the subsequent operations of transfer and/or treatment of the polymer but can also allow to avoid the granulation step of polymer. This operation, as it is known, requires large amounts of energy.

The methods employed until now for the preparation of catalysts having a controlled morphology and/or particle  
30 size are based on operations expensive per se, which comprise the preformation of a precursor of the catalytic com  
35 ponent in form of particles having a controlled morphology and the subsequent transformation of these particles to obtain the true catalyst component or the precipitation of

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5 the catalyst component under conditions in general very critical, followed by the steps of separation, washing and drying of the solid.

10 According to other methods, precursors of the catalyst component in the melted state are emulsified in an inert immiscible liquid and the emulsion is then subjected to quenching to obtain the solidification of the dispersed liquid phase which is subsequently treated for the transformation thereof to catalyst component.

15 Examples of these methods are described in the applicant's U.S. patent 3,953,414 and Belgian patent 878,347.

20 Coordination catalysts are not known hitherto wherein the component comprising the transition metal compound in the form of a liquid immiscible in the conventional polymerization solvents, is employed in emulsion or dispersion in said liquid medium.

25 It has been now unexpectedly found that it is possible to obtain polymers of ethylene and copolymers thereof with olefins in the form of particles having controlled morphology and/or particle size, by carrying out the polymerization with catalysts obtained from emulsions or dispersions in an inert liquid medium or in an inert gas phase of a liquid phase immiscible in the liquid medium, comprising a  
30 compound or compositions containing a transition metal compound of the Groups IV to VI of the Periodic System, that are immiscible, in the liquid state, with the normal aliphatic hydrocarbons.  
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5       The catalyst components of the invention consist in particular of emulsions or dispersions in an inert liquid medium or in an inert gas phase of a liquid phase comprising compounds or compositions containing compound of Ti, V, Zr and Cr, in particular compounds of Ti, that are immiscible  
10 in the normal aliphatic hydrocarbons (hexane, heptane and the like). Within the scope of the invention fall also the liquid or solid catalytic components obtained by post-treatment of the catalytic emulsions or dispersions of the inven-  
15 tion.

Also the solid or liquid catalyst components form part of the invention, that are obtained by subjecting to transformation post-reactions in order to obtain the true catalytic  
20 component emulsions or dispersions in an inert liquid medium or in an inert gas phase of precursors of catalyst components, the precursors being immiscible, in the liquid state, in the normal aliphatic hydrocarbons.

25       According to another aspect of the invention the transition metal compound immiscible in aliphatic hydrocarbons or the liquid precursor are made to be adsorbed on solid porous supports having a controlled morphology and/or particle size: the support is then used in suspension in an inert li-  
30 quid medium immiscible with the adsorbed liquid phase or dispersed in gas phase.

Examples of solid inert supports are silica, alumina and polymers in form of porous particles having controlled  
35 morphology and/or size.

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5 As already indicated, any transition metal compound of the Groups IV to VI that is immiscible in the liquid state with aliphatic hydrocarbons is suitable for the preparation of the emulsions or dispersions forming the catalytic components of the invention.

10 Similarly, any precursor of the catalytic components which is immiscible, in the liquid state, with the aliphatic hydrocarbons may be used to prepare the emulsions or dispersions useful for the preparation of the catalytic components of the invention, such as the reaction product of an  
15 anhydrous magnesium halide, in particular  $MgCl_2$  of a Mg dialkyl or a Grignard reagent, with an anhydrous aluminum halide, in particular  $AlCl_3$ , in an aromatic hydrocarbon in particular toluene, in the presence of a halogenated hydrocarbon, preferably 1,2-dichloroethane. To the oily liquid  
20 thus obtained (non immiscible in the same aromatic hydrocarbon), a titanium compound, in particular  $TiCl_4$  is added. An oily liquid is obtained that is immiscible in the normal  
25 aliphatic hydrocarbons.

More particularly, the Mg and Al halides and the aromatic hydrocarbon are caused to react at the reflux temperature of the hydrocarbon in the Mg/Al/toluene molar ratio of  
30 1:2:12.

To this suspension the halogenated hydrocarbon is added in the ratio of about 2 mols per mol of Mg halide and it is heated until an oily liquid is formed. Then the Ti compound  
35 is added in a Ti halide/Mg halide comprised in generale between 0.1:1 and 1:1.

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5 In the above preparation the halogenated hydrocarbon can  
be replaced by anhydrous gaseous hydrochloric acid or by a  
normally liquid halogenated transition metal compound. For  
example  $\text{TiCl}_4$  is particularly suitable to this purpose. In  
10 the latter case no further addition of the transition metal  
compound is needed to prepare the catalyst component.

According to another embodiment of the invention the Mg  
dihalide can be added last and solubilized in the mixture  
obtained by first mixing  $\text{AlCl}_3$  and toluene and by there-  
15 after treating the mixture with the halogenated hydrocarbon  
or gaseous  $\text{HCl}$  or  $\text{TiCl}_4$ .

The oily liquid that is obtained before the addition of  
the Ti compound is in itself a precursor of the catalytic  
20 components that can be emulsified and the emulsion can be  
treated for the transformation thereof to the catalyst com-  
ponent.

In the above indicated preparation the Al trihalide can  
25 be substituted by an alkyl Al-dihalide, the toluene by ben-  
zene, xylene and by similar aromatic hydrocarbons; 1,2-di-  
chloroethane can be substituted by  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_3\text{H}_7\text{Cl}$ ,  $n\text{-C}_4\text{H}_9\text{Cl}$ ,  
 $s\text{-C}_4\text{H}_9\text{Cl}$ ,  $t\text{-C}_4\text{H}_9\text{Cl}$ ,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and by  
alike alkyl, aryl or arylalkyl halides.

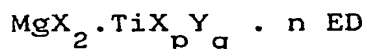
30 Another method of preparation consists in dissolving an  
anhydrous Mg halide in a Ti tetraalcoholate, in particular  
Ti tetrabutylate, and in flowing an anhydrous gaseous hydro-  
halogenic acid through the solution until an oily phase is  
35 separated. According to a modification of the above describ

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5 ed method, the hydrohalogenic acid can be replaced by an acyl chloride, in particular acetyl chloride. The butyl acetate that is formed is partly removed until formation of an oily liquid.

10 Other compounds suitable for the preparation of the catalytic components of the invention can be selected from the compounds having the formula:



15 that in the liquid state are immiscible with aliphatic hydrocarbons. In the formula X is a halogen atom; Y is a OR radical in which R is an alkyl, cycloalkyl or aryl group containing from 1 to 18 carbon atoms; p is a number from 1 to 4; q is a number from zero to 3; p+q = 4; n is a number from 3 to 6; ED is an electron-donor compound selected in particular from the esters of carboxylic aliphatic or aromatic acids.

25 Examples of these compounds are:  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 4 \text{ Ac}$  (AC =  $\text{CH}_3\text{COOC}_2\text{H}_5$ ),  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 4 \text{ EB}$  (EB = ethylbenzoate),  $\text{MgCl}_2 \cdot \text{TiCl}_2(\text{OC}_2\text{H}_5)_2 \cdot 4 \text{C}_2\text{H}_5\text{OH}$ ;  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 5 \text{POCl}_3$ .

30 These compounds are prepared according to known methods, by dissolving the Mg halide in the ED compound, by adding to the solution the stoichiometric amount of the Ti compound and then by causing the reaction to take place at reflux. The excess of the ED compound is at the end removed by evaporation.

35 As already indicated, the compounds or the compositions

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5 containing the transition metal compounds, which form the emulsions or dispersions of the invention, can be subjected to modification or transformation reactions before that the emulsions or dispersions are employed as catalyst component. Said reactions comprise the reactions with electron-donor  
10 compounds, in particular esters, Al-alkyl compounds and silicon compounds.

The emulsion is then made to react, according to known methods, with reagents capable to transform the adduct in  
15 active catalytic component.

Known transformation reactions to catalyst component are those wherein the adduct is made to react with  $\text{TiCl}_4$  or with an Al-alkyl compound or with halogenated silicon  
20 compounds such as  $\text{SiCl}_4$  and halosilanes. Examples of these reactions are described in the Belgian patents 857,574 and 878,347.

As already indicated, the oily liquid obtained from the reaction of  $\text{MgCl}_2$ ,  $\text{AlCl}_3$ , toluene and dichloroethane can be  
25 utilized as precursor and made to react in emulsion or dispersion with substances capable to transform it to the catalyst component. For example it can be reacted with  $\text{TiCl}_4$  and alkyl hydropolysiloxanes, according to known  
30 methods.

The emulsifying of the transition metal liquid compounds as well as that of the precursors is carried out according to known techniques.

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5 The liquid compounds can be dispersed in the same hydro-  
carbon medium used in polymerization, optionally in the pre-  
sence of surfactants of known type selected from those that  
are inert or poorly reactive toward the catalyst components.  
10 In the processes in gas phase, the transition metal com-  
pound can be dispersed directly in the gas phase containing  
the co-catalyst.

15 Preferably, however, the transition metal compound is  
dispersed previously into an oil of parafinic, naphthenic,  
aromatic or siliconic type; the resulting dispersion or  
emulsion is then fed to the polymerization reactor contain-  
ing the co-catalyst.

20 Examples of these oils are silicon oil Baysilon M 100  
(Bayer), vaselin O 55 (Rol), Cortis M 100 oil (Total),  
Circosol 2XH oil (Sunoco) and Dutrex R55 oil (Shell).

25 The addition during the emulsifying of an electron-do-  
nor compound and/or of the co-catalyst in amounts in gene-  
ral comprised between 5 and 50% by weight on the amount of  
the transition metal compound has beneficial effects on the  
morphologic characteristics of polymer.

30 In some cases, in particular when the emulsion are un-  
stable in the time or would create feeding problems, it has  
been found convenient to prepolymerize small amounts of  
ethylene or other olefin. The prepolymerization is carried  
out in general until a few grams of polymer per gram of ca-  
talyist component are formed.

35 A solid stable prepolymer is obtained having spherical

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5 and regular size particles which subsequently during the polymerization maintain or reproduce the shape while growing, thus generating polymer particles that are also regular and spherical.

10 The co-catalysts to be utilized together with the catalytic components of the invention are the organometal compounds of Al, preferably the not halogenated compounds, as for example  $\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{Al}(\text{iC}_4\text{H}_9)_3$ ,  $\text{Al}(\text{n-C}_4\text{H}_9)_3$ ,  $\text{Al}(\text{C}_4\text{H}_9)_2\text{H}$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ . The polymerization of ethylene or of mixtures  
15 thereof with alpha-olefins with these catalysts is carried out according to any of the known techniques, in the presence or the absence of hydrocarbon media, in liquid or gas phase, at temperatures preferably comprised between 0° and  
20 200 °C and by operating in general in the presence of molecular weight regulators of polymer, as hydrogen.

Al already indicated, the catalysts are used in the polymerization of both ethylene and of mixtures thereof with  
25 alpha-olefins,  $\text{C}_3\text{-C}_{12}$ , in particular butene, to obtain crystalline copolymers of ethylene containing minor amounts of polymerized alpha olefins as well as to obtain elastomeric ethylene-alpha-olefin copolymers, in particular ethylene-propylene copolymers containing optionally insaturations  
30 derived from polyenes having at least two double bonds.

In using the emulsified or dispersed catalyst component of the invention, precautions have to be taken to introduce the catalyst component into the polymerization reactor  
35 in the form of the emulsion or dispersion as prepared. Means

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5 to avoid the demixing of the dispersed or emulsified liquid  
phase are well known in the art. For instance, the emulsi-  
fied or dispersed catalyst components should be introduced  
into the polymerization reactor under the polymerization  
conditions as quickly as possible, immediately after its  
10 preparation.

As mentioned at the beginning, the advantages obtain-  
able with the use of these catalysts are multiple. These  
catalysts, besides being endowed of activities in general  
15 very high (such as to not require any purification treat-  
ment of the obtained polymer from the catalytic residues),  
show the advantage of furnishing polymer powders endowed  
of excellent morphological characteristics, high bulk densi-  
ty and very restricted particle size distribution. Conse-  
20 quently, the polymers possess a so high flowability and  
bulk density that they can be utilized directly in the con-  
ventional operations of molding and extrusion, without hav-  
ing recourse previously to a costly granulation operation.

25 Another advantage of remarkable interest is the extreme  
simplicity of preparation of these catalysts, which reduces  
considerably the cost thereof, also with respect to other  
known, highly active catalysts.

30 The melt index E and respectively N were determined  
according to the ASTM methods D-1238 condition E and respec-  
tively N, measured at 190 °C and expressed in g/10 minutes.

The tamped bulk density was determined according to a  
35 method described in DIN 53194.

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5 The particle size was determined according to ASTM  
D 1921-63.

The flowability and the poured bulk density were determined according to ASTM D-1895-69.

10 The following examples are given to illustrate the invention without limiting it.

#### Examples 1-8

##### Preparation of catalytic component A.

15 The catalyst component A used in all tests of examples 1-8 was prepared in the conditions and with the modalities as follows.

20 9.5 g (0.1 mol) of anhydrous powdered magnesium chloride (water content lower than 1% by weight), 39.9 g (0.3 mol) of anhydrous aluminum trichloride, and 128 cc of anhydrous toluene were introduced in said order into a 500 cc flask fitted with mechanical stirrer, dropping funnel, reflux  
25 condenser and thermometer, that was previously flushed with nitrogen.

The resulting toluene suspension was heated to 110 °C and maintained under stirring at this temperature for 2 hours. The mixture was then cooled to 45 °C and 15.7 cc of 1,2-di  
30 chloroethane were added thereto with the dropping funnel.

After heating at 100 °C for 1 hour, a red-brownish liquid was obtained, to which, after cooling again to 45 °C, 0.1 mol of  $\text{TiCl}_4$  was fed.

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5 After an additional 15 minutes stirring at 45 °C, the solution obtained results to have a volume of 178 cc and the following composition:

Ti = 2.35% by weight

Al = 4.5 % by weight

10 Cl = 22.75% by weight

Mg = 1.2 % by weight

The viscosity at 20 °C was 3.5 centistokes. The density at 20 °C was 1.13 g/cc.

15 Dispersion of catalytic component A.

The apparatus for the dispersion or emulsifying of the catalytic components that was used in all examples consists of a small turbostirrer (Ultra Turrax TP 18/10 manufactured by Janke & Kunkel, Ika-  
20 werk, Staufen) turning at a speed of 12,000 r.p.m. that was inserted in a 150 cc Keller type flask fitted with a 50 cc graduated dropping funnel and a thermometer. The control of the temperature was carried out by immersion of the flask in a methanol /dry ice  
25 cooling system.

Prior to use, the apparatus was flushed with nitrogen. The dispersing oil, the optional additives coadjuvant for the dispersion were introduced in this order into the  
30 flask, and the catalytic component was then introduced in the time of 5 minutes under the highest stirring while simultaneously cooling and maintaining the temperature at 20 °C. The stirring was then continued for another 10 minutes.  
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At the end of the dispersion operation and after reducing to 50% the stirring speed, the emulsion obtained was injected in the polymerization autoclave in the amounts reported in Table 1.

#### Polymerization of ethylene

The polymerization test of all examples was carried out in a 2.5 liter stainless steel autoclave fitted with an elicoïdal blade stirrer operating at the speed of 600 r.p.m. and with an automatic thermostatic system.

At the moment of introducing the catalytic dispersion the autoclave duly flushed with nitrogen contains already 1 liter of anhydrous hexane and 7.5 mMols of Al-triisobutyl that are maintained under stirring at 60 °C. After introduction of the catalytic component in the hexane, the temperature was raised to 75 °C, 3 atm. of H<sub>2</sub> (partial pressure) were introduced and lastly the autoclave was pressurized with ethylene up to the total pressure of 14 atmospheres. The autoclave was then stirred for 2 hours while maintaining constant the pressure by continuous feeding of ethylene. The feed of ethylene was discontinued, the reactor was cooled to room temperature, the polymer was discharged and separated from hexane by filtration and then dried in nitrogen flow at 70 °C for 8 hours.

The amounts of the reactants used in the preparation of the dispersions of the catalytic component in the different types of oil and the polymerization results are reported in Table 1.

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5 In Example A of Table 1 are reported the results of the polymerization of ethylene with the catalytic component A as such (not subjected to emulsifying).

10 Examples 9-15

Preparation of the catalytic component B

The catalytic component B utilized in examples 9-15 was prepared under the conditions and with the operating modalities as follows.

15 0.2 mols of anhydrous powdered magnesium chloride and 0.4 mols of titanium tetrabutylate were introduced into a 1000 cc flask fitted with mechanical stirrer, reflux condenser, thermometer and dropping funnel. The flask was heated at 20 140 °C for 3 hours.

The resulting solution, cooled to 60 °C, was diluted with 640 cc of anhydrous n-heptane. Then gaseous anhydrous hydrochloric acid was introduced by means of a glass tube immersed directly in the liquid phase at 20 °C and under stirring, 25 in such amount as to maintain the temperature of the system at about 30 °C.

During this treatment, there takes place first a turbidness of the solution and then the separation of an oily reddish phase immiscible in heptane. 30

After 3 hours the feed of hydrochloric acid was interrupted and the oily suspension was heated while stirring at 60 °C for 30 minutes. Said liquid suspension was transferred at 35 room temperature to a dropping funnel and then the oily

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5 phase was separated. 206 cc of oily liquid were obtained which had the following composition by weight:

Ti	=	7.4 %
Mg	=	1.75 %
Cl	=	22.15 %
C <sub>4</sub> H <sub>9</sub> OH	=	45.7 %

10 The viscosity at 20 °C is of 180 cst and the density at 20 °C is of 1.056 g/cc. For the dispersion or emulsifying of the catalytic component B in the different types of oil and for the experimenting with it, including the polymeri-  
15 zation tests therewith, the same operating modalities already described for the catalytic component A were adopted. The results were reported in Table 2.

20 In Example B of Table 2 the results of polymerization of ethylene using the catalytic component B as such (not dispersed) were reported.

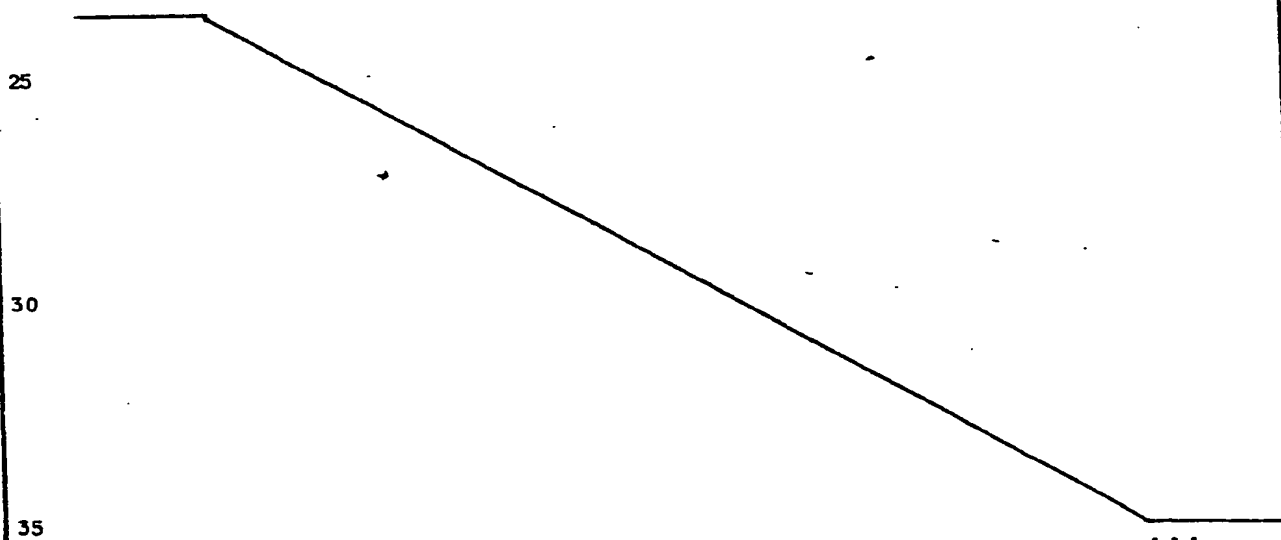


Table 1

EXAMPLE N°		A	1	2	3	4	5	6	7	8		
DISPERSION OF THE CATALYTIC COMPONENT	DISPERSING AGENT	Type	-	BAYSILON M 100 oil	BAYSILON M 100 oil	BAYSILON M 100 oil	BAYSILON M 100 oil	VASELIN OB 55 oil	CORTIS M 100 oil	CIRCOSOL 2XH oil	DUTREX R 55 oil	
		Viscosity at 20 °C(cst)	-	140	140	140	140	55	500	91.5	175 (100 °C)	
		Quantity (cc)	-	20	15	20	20	20	20	20(1)	20(1)	
		ADDITIVE	Type	-	-	-	n.butyl ether	4mM A(1sc butyl)+n. butyl ether	-	-	-	-
	Quantity (cc)		-	-	-	3	3	-	-	-	-	
	Catalytic liquid A (cc)	-	20	30	20	20	20	10	10(1)	10(1)		
	Dispersed catalyst used (cc)	0.3	0.5	0.15	0.3	0.3	0.3	0.1	0.15	0.3		
	Weight polymer obtained (g)	239	135	198	205	183	121	185	270	104		
	Yield(g.pol./g.TI).10 <sup>-3</sup>	30	20	75	55	49	30	209	203	39		
	Melt Index E (g/10')	0.21	0.4	0.45	0.5	0.21	0.25	0.35	0.23	0.14		
RESULTS	Melt Index N Melt Index E		10.7	8.1	9.2	8	7.6	11.6	8.3	8.9	7.2	
	Tamped bulk density (g/cc)		0.25	0.39	0.27	0.41	0.43	0.27	0.35	0.23	0.18	
	POLYMERIZATION	POLYMER MORPHOLOGY	Spherical polymer	NO	YES	YES	YES	YES	YES	YES	NO	YES
			Particle form polymer	NO	NO	NO	NO	NO	NO	YES	YES	NO
			Irregular polymer in powder	YES	NO	NO	NO	NO	YES	NO	NO	YES

(1) Dispersion carried out at 50 °C.

EXAMPLE		N°	B	9	10	11	12	13	14	15
DISPERSION OF THE CATALYTIC COMPONENT	DISPERSING AGENT	Type	-	BAYSILON M100 oil	BAYSILON M 100 oil	VASELIN OB 55 oil	CORTIS 100 M oil	CIRCOSOL 2XH oil	DUTREX R 55 oil	n-HEPTA- NE
		Viscosity at 20 °C (cst)	-	140	140	55	500	91.5	17.5 (100°C)	0.57
		Quantity (cc)	-	20	10	20	20	20	20	50
	ADDITIVE	Type	-	-	Al(n-octyl) <sub>3</sub>	-	-	-	-	FENOROL 10
		Quantity (cc)	-	-	3.7 (m.mol/g)	-	-	-	-	0.03 (g)
	Catalytic liquid B (cc)		-	20	20	10	10	10	10	10
	Dispersion used (cc)		0.01	0.01	0.02	0.05	0.03	0.05	0.05	0.02
	Weight polymer obtained (g)		154	91	178	123	234	268	91	103
	Yield (g.pol./g Ti) x 10 <sup>-3</sup>		197	233	171	95	299	206	70	396
	Melt Index E (g/10')		0.25	0.3	0.25	0.15	0.18	0.23	0.2	0.12
POLYMERIZATION RESULTS	Melt Index N Melt Index E		8	8.1	7.8	8.0	10	7.4	8	7.5
	Tapped bulk density (g/cc)		0.35	0.33	0.35	0.22	0.24	0.28	0.23	0.21
	POLYMER MORPHOLOGY	Spherical polymer	NO	NO	YES	YES	YES	YES	YES	YES
		Particle form polymer	NO	YES	NO	YES	YES	NO	YES	YES
		Irregular polymer in powder	YES	YES	NO	NO	NO	YES	NO	NO

Examples 16 and 17Preparation of the catalytic component C.

The catalytic component C utilized in examples 16 and 17 was obtained in the following manner.

0.2 mols of anhydrous powdered  $\text{MgCl}_2$  and 0.16 mols of titanium tetrabutylate were introduced in this order into a 250 cc flask fitted with mechanical stirrer, reflux condenser and thermometer.

The flask was heated while stirring the suspension at 140 °C for 3 hours. A milky liquid was obtained, to which, after cooling to room temperature, 1.2 mols of acetyl chloride were added in 30 minutes. The obtained suspension while still under stirring was heated at boiling (73 °C) for 2 hours.

Then the unreacted acetyl chloride was removed by distillation. The temperature in the flask is let raise up to 125 °C. At this point the residue has the appearance of an oily red-brownish mass.

It amounts to 90 cc and has a density of 1.25 g/cc at 20 °C. The results of the polymerization tests were reported in Table 3. Test C was carried out using the catalytic component C not dispersed.

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Table 3

DISPERSION OF THE CATALYTIC COMPONENT		EXAMPLE N°	C	16	17	
DISPERSING AGENT	Type		-	BAYSILON M 100 OIL	CORTIS M 100 OIL	
	Viscosity at 20 °C (cst)		-	140	500	
	Quantity (cc)		-	20	20	
	Catalytic liquid C (cc)		-	10	10	
POLYMERIZATION RESULTS	Catalytic dispersion used (cc)		0.2	0.3	0.2	
	Weight polymer obtained (g)		287	182	230	
	Yield (g.pol/g Ti).		16,000	20,000	38,000	
	Melt Index E (g/10')		0.07	0.07	0.07	
	Melt Index N Melt Index E		10.2	9.7	9.3	
	Tamped bulk density (g/cc)		0.23	0.27	0.28	
	POLYMER MORPHOLOGY	Spherical polymer		NO	YES	YES
		Particle form polymer		NO	YES	YES
		Irregular polymer. in powder		YES	NO	NO

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Example 18

The following substances were used for the preparation of the dispersion of the catalytic component:

Baysilon M 100 oil = 30 cc

n-butyl ether = 4.5 cc

Catalytic component A = 30 cc

The resulting dispersion was introduced into a 2.5 l reactor containing already 1000 cc of anhydrous hexane and 0.1 mol of aluminum triisobutyl at the temperature of 40 °C.

Ethylene was then introduced till a pressure of 0.6 atm. The polymerization starts immediately and causes a temperature increase to 45 °C.

While maintaining constant said conditions, ethylene was continuously fed for 30 minutes, i.e. until about 3 g of ethylene are polymerized per gram of catalytic component A. The pre-polymerized catalytic component was then discharged and, after removal of the solvent by filtration, it was subjected to two washings with anhydrous hexane at room temperature.

The catalytic component in hexane suspension was then used in subsequent tests of ethylene polymerization, in order to evaluate the possible variations in performance with respect to the time (ageing).

In table 4 the results of said tests (ageing of the prepolymerized catalysts: zero days; 5 days; and 13 days) were reported.

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5 Furthermore, some morphological characteristics of the polymers obtained (flowability and particle size distribution) were reported.

In all cases the powders obtained consisted wholly of spherical particles.

10 In the case of the polymer obtained with aged catalyst, the analysis of the catalytic residues furnished the following results:

15	Ti	=	2	ppm
	Cl	=	<25	ppm
	Mg	=	4.6	ppm
	Total ashes	=	0.095%	

20 The polymerization test was carried out in the conditions of examples 1-8 with the difference that the duration is of 4 hours in place of 2 hours.

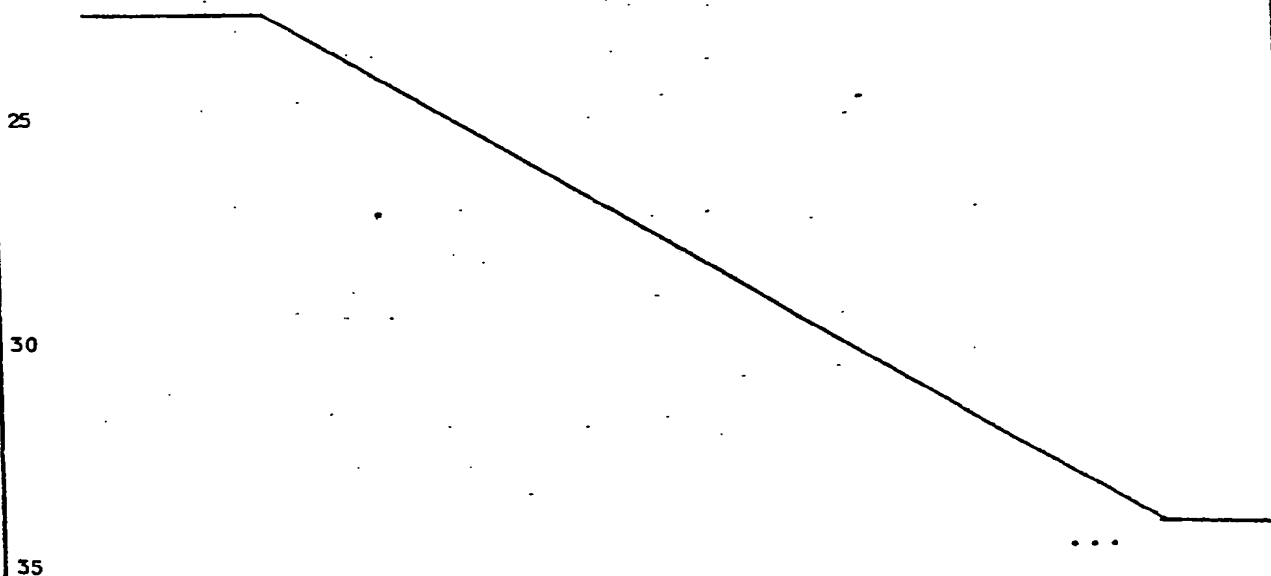


Table 4

Ageing of the prepolymerized catalyst		zero days	5 days	13 days
Yield (g polymer/g Ti).		313,000	340,000	315,000
Melt Index E (g/10')		0.23	0.14	0.2
<u>Melt Index N</u> Melt Index E		8	8.3	8.3
Tamped bulk density (g/cc)		0.4	0.41	0.4
Flowability (sec.)		17.5	17	18
PARTICLE SIZE DISTRIBUTION (% BY WEIGHT)	> 1000 $\mu$ (and < 2000 $\mu$ )	25.1	30.4	30.2
	> 500 $\mu$ %	53.3	52.1	54
	> 177 $\mu$ %	19.7	16.7	15
	> 105 $\mu$ %	1.6	0.5	0.5
	< 105 $\mu$ %	0.3	0.3	0.3



Example 19

5 300 g of polyethylene obtained according to example 18 (ageing time of 5 days) were introduced into a 3 liter stain less steel autoclave fitted with an anchor-shaped stirrer.

10 After heating at 80 °C for 1 hour under a flow nitrogen and under stirring at intervals, the polymer was subjected to treatment with 0.5 g of aluminum triisobutyl diluted in 500 g of propylene. The mixture was stirred at 70 °C for 2 hours and then all propylene was removed slowly.

15 0.634 g of prepolymerized catalyst (obtained as described in example 18) and then, at the temperature of 60 °C, 1 g of aluminum triisobutyl dissolved in 20 cc pentane were charged into the reactor.

20 The reactor was heated at 75 °C and while maintained under stirring was charged with 1.8 atm. of hydrogen and then with ethylene up to a total pressure of 9 atm. The pressure was maintained constant during the polymerization by continuous addition of ethylene.

25 After 4 hours, the reactor was degassed and the dry polymer was collected which weighed 578 g. The yield was 231,000 g polymer/g titanium used.

The morphology of the obtained polymer was wholly spherical.

30 The tamped bulk --- density was 0.38 g/cc. The flowability was 18 seconds.

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The particle size distribution was as follows:

5	$\emptyset > 1000 \mu$ (and $< 2000 \mu$ )	= 33.5 % by weight
	$\emptyset > 500 \mu$	= 59.4 % by weight
	$\emptyset > 177 \mu$	= 6.6 % by weight
	$\emptyset > 105 \mu$	= 0.4 % by weight
10	$\emptyset < 105 \mu$	= 0.1 % by weight

#### Example 20

Two polymerization tests were carried out, one in hexane and the other in isobutane, and both were carried out in the presence of butene-1 in different amount.

In the two tests it was utilized a prepolymerized catalyst from the same preparation used for the polymerizations reported in Table 4, except that it had 90 days of ageing.

The autoclave used was entirely similar to that of the preceding polymerization, except that it had a 1.5 l capacity in place of 2.5 l.

#### Polymerization in hexane

Anhydrous hexane containing Al-triisobutyl and the weight catalyst were charged into the autoclave duly flushed with nitrogen.

The reactor was heated at 70 °C and then flowed with hydrogen and pressurized with the same up to 3 atmospheres. Simultaneously 18 g of butene-1 and ethylene up to a total pressure of 14 atmospheres were introduced. The pressure was maintained constant by introducing continuously ethylene-

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5 ne and butene, the latter one in an amount of 0.6 g per each 30 g of ethylene fed.

After 2 hours polymerization, the reactor was degassed and cooled by stripping with steam. The polymer was recovered from the slurry and then dried at 70 °C in a nitrogen flow  
10 for 12 hours.

Polymerization in isobutane.

20 cc hexane containing the catalyst and Al-triisobutyl we-  
15 re charged into the flushed autoclave wherein a flow of iso-  
butane is maintained. Then also isobutane in liquid state  
was introduced. The reactor was heated at 70 °C (isobutane  
pressure = 10 atm.). 4 atmospheres of hydrogen were introduc-  
20 ed therein and simultaneously 180 g of butene-1 and ethyle-  
ne up to a total pressure of 29.5 atmospheres. The polymere-  
rization was continued in these conditions for 2 hours, by  
adding 2.95 g of butene-1 per each 30 g of ethylene fed.

25 The reactor was degassed and cooled to room temperature. The  
polymer was recovered and dried at 70 °C in a nitrogen flow  
for 12 hours.

The data concerning both tests and the results were report-  
ed in Table 5.

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Table 5

Polymerization in		hexane	isobutane
Hexane (cc)		700	20
Isobutane (g)		-	220
Al-triisobutyl (g)		1	1
Prepolymerized catalyst (g)		0.3	0.625
Butene-1 (g)	{ initial feed	18	180
	{ total feed	19.2	194.75
Obtained polymer (g)		65	175
Yield (g/g Ti)		114,000	147,000
Melt index E (g/10')		0.17	1.6
N/E		10.6	7.6
F/E		31.2	25.6
Bonded butene (% by weight)		< 2	4.5
Density (g/cc)		0.9394	0.9262
Bulk density (Tamped) (g/cc)		0.31	0.33
Flowability of the polymer (sec.)		23	24.4
PARTICLE SIZE	Morphology	wholly spherical	wholly spherical
	> 2000 $\mu$ (% by weight)	0.9	1.4
	> 1000 $\mu$ (% by weight)	26.1	23
	> 420 $\mu$ (% by weight)	52.9	57.2
	> 250 $\mu$ (% by weight)	12.8	12.3
	> 149 $\mu$ (% by weight)	5.3	4.4
	> 105 $\mu$ (% by weight)	1.2	1.0
	< 105 $\mu$ (% by weight)	0.8	0.7

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5 Excluding silicon oil, the carbon of the chemical structures of the dispersing oils used in examples 5 and 11, respectively 6 and 12; 7 and 13; and respectively 8 and 14 is distributed percentwise as follows:

10

Oil	Aromatic carbon	Naphthenic carbon	Paraffinic carbon
Vaselin OB 55	-	-	100
15 Cortis 100 M	7	28	65
Circosol 2XH	20	39	41
Dutrex R 55	49	35.5	17.5

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25 Example 21

60 cc of Baysilon M 100 silicon oil and 2.4 g of anhydrous magnesium chloride were introduced in this order into a 200 cc Keller type flask fitted with a turbostirrer of the type used in examples 1-8 and of a dropping funnel. 4.35 cc of anhydrous ethanol were added slowly to the mixture. The suspension was heated slowly to 80 °C and then to 125 °C after inserting on the Keller a reflux condenser in order to stop the evolution of ethanol vapours.

30 The emulsifying of the adduct  $MgCl_2$ .alcohol that is formed, was obtained by vigorous stirring. 300 cc of ISOPAR G and 8.25 cc of  $TiCl_4$  were introduced into a glass vessel with

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5 jacket for the circulation of a thermostatic liquid, and fitted with mechanical stirrer, reflux condenser and thermometer.

The temperature of the solution was increased to 120 °C and at said temperature the whole volume of the emulsion obtained as indicated was introduced therein slowly (about 5 minutes).

The whole system was maintained at 120 °C for 1 more hour. After removing the liquid by siphoning, the solid was washed with hot ISOPAR G. A sample containing 0.004 g of solid catalytic component was taken from the suspension of the last washing and it was used in a polymerization test of ethylene that was carried out in the conditions described in examples 1-8.

20 50 g of polymer (yield of 12,500 g/g catalytic component) were obtained in the form of particles having a controlled particle size (most of the particles have the size comprised between 500 and 1000 micron).

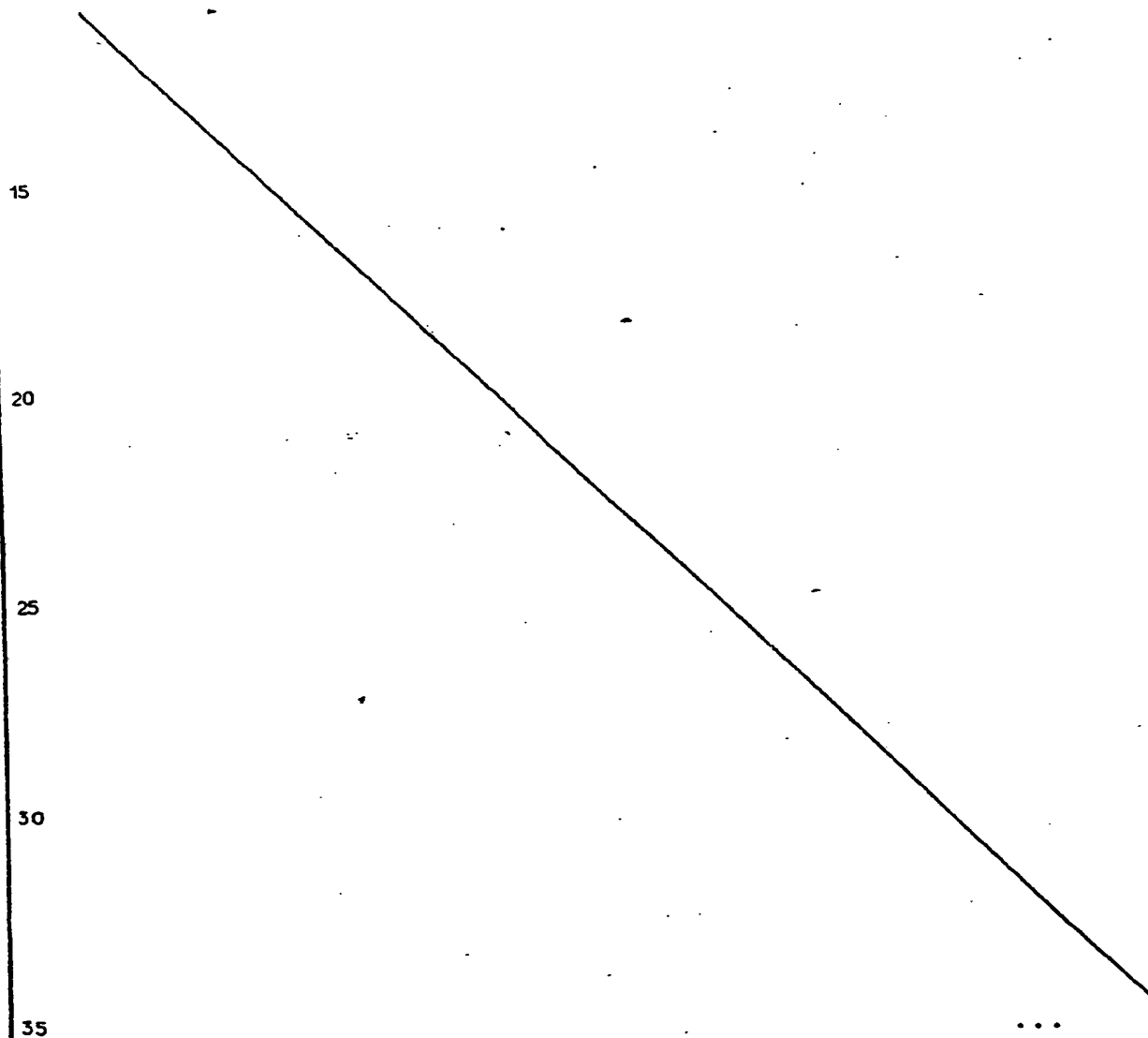
#### 25 Example 22

Example 21 was repeated except that the emulsion of the adduct of  $\text{MgCl}_2$  and ethanol was added to a solution of 8.3 cc of  $\text{TiCl}_4$  in 300 cc of ISOPAR G that is maintained at 120 °C. At about a half way of addition of the emulsion, another 8.3 cc of  $\text{TiCl}_4$  were added, and the addition of the emulsion was then completed.

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5 In a polymerization test carried out in the conditions of  
example 21 and using 0.0055 g of catalytic component,  
120 g of polymer were obtained in the form of spheroidal  
10 particles having the size mainly comprised between 500  
and 1000 micron.



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- 1) Components of catalysts for the polymerization of ethylene and of mixtures thereof with olefins, in form of emulsions or dispersions in an inert liquid medium or in inert gas phase of a liquid phase comprising a compound or a composition containing a transition metal compound of the Group IV-VI of the Periodic System, immiscible with aliphatic hydrocarbons, or that are obtained by subjecting to transformation reactions forming the catalyst component, emulsions or dispersions in an inert liquid medium or in inert gas phase of a precursor of the catalyst component, that is immiscible with aliphatic hydrocarbons.
- 2) Catalyst components according to claim 1, in which the transition metal compound is selected from the compounds of Ti, V, Zr and Cr.
- 3) Catalyst components according to the preceding claims, in which the dispersed liquid phase comprises compounds of Ti and Mg.
- 4) Catalyst components according to claim 3, in which the dispersed liquid phase containing the Ti and Mg compound is obtained by reacting an anhydrous halide of Ti and Mg and an aluminum halide or alkylidihalide in an aroma-

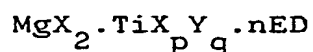
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5       tic liquid hydrocarbon, in the presence of a halogenat-  
ed hydrocarbon or by reacting an anhydrous halide of  
Mg and a Ti alcoholate, in the presence of an anhydrous  
hydrohalogenic acid.

- 10       5) Catalyst components according to claim 3, in which the  
Ti and Mg compound has the formula:



15       wherein X is a halogen; Y is a radical OR (R = Alkyl,  
cycloalkyl or aryl group containing from 1 to 18 car-  
bon atoms); p is a number from 1 to 4; q is a number  
from 0 to 3; p+q = 4; n is a number from 3 to 6; ED is  
an electron-donor compound.

- 20       6) Catalyst components according to the preceding claims,  
in which the compound or composition containing the  
transition metal compound is subjected to reactions  
and/or to modifying treatments before the use of the  
25       emulsion or dispersion as catalyst component.

- 30       7) Catalyst components according claim 6, in which the  
emulsion or dispersion is reacted with compounds se-  
lected from the Al-alkyl compounds, preferably in the  
presence of an olefin or from the silicon compounds  
and the electron-donor compounds.

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- 5        8) Catalyst components according to claim 1, in which the precursor of the catalytic component is a compound or a composition containing a Mg compound.
- 10       9) Catalyst components according to claim 8, in which the Mg compound is selected from the adducts of a Mg halide with an electron-donor compound, preferably an aliphatic, cycloaliphatic or alkylaryl alcohol.
- 15       10) Catalyst components according to claims 8 and 9, in which the emulsion or dispersion of the precursor of the catalytic component is reacted with a compound selected from the Ti halides, the Al-alkyl compounds
- 20       and the halogenated Si compounds.
- 25       11) A catalyst component according to claim 1, in which the aliphatic hydrocarbon-immiscible liquid compound of the transition metal is adsorbed on solid porous supports having a controlled morphology and/or particle size.
- 30       12) Catalysts for the polymerization of ethylene and of the mixtures thereof with alpha-olefins which comprise the reaction product of an organometal compound of Al and a catalyst component according to preceding claims 1 to 11.
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European Patent  
Office

# EUROPEAN SEARCH REPORT

0083074  
Application number

EP 82 11 1904

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D,A	US-A-3 953 414 (P.GALLI et al.) *Claims 1-13*	1	C 08 F 10/02 C 08 F 4/62
A	EP-A-0 018 737 (MITSUI) *Claims 1-12*	1	
A	FR-A-2 428 056 (MITSUBISHI) *Claims 1-6; example 1*	1	
A	US-A-4 218 339 (U.ZUCCHINI AND I CUFFIANI) *Claims 1-21; column 2, lines 52-68*	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30-03-1983	Examiner WEBER H.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</div> <div>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</div>			

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